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(54) Title: PROCESS FOR MINERAL CARBONATION WITH CARBON DIOXIDE

(57) Abstract: A process for mineral carbonation with carbon dioxide wherein carbon dioxide is reacted with a bivalent alkaline earth metal silicate, selected from the group of ortho-, di-, ring, and chain silicates, which silicate is immersed in an aqueous electrolyte solution. The invention further relates to the use of the mixture of carbonate and silica formed in such a process in construction materials and to the use of the carbonate formed by such a process for the production of calcium oxide.

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PROCESS FOR MINERAL CARBONATION WITH CARBON DIOXIDE

The present invention relates to a process for mineral carbonation with carbon dioxide, to the use of the mixture of silica and carbonate formed in such a process in construction materials and to the use of the carbonate formed in such a process in the production of calcium oxide.

The rising of the carbon dioxide concentration in the atmosphere due to the increased use of energy derived from fossil fuels potentially has a large impact on climate change. Measures to reduce the atmospheric carbon dioxide concentration are therefore needed.

In nature, stable mineral carbonate minerals and silica are formed by a reaction of carbon dioxide with natural silicate minerals:

$$(Mg,Ca)_xSi_yO_{x+2y} + xCO_2 \Rightarrow x(Mg,Ca)CO_3 + ySiO_2$$

The reaction in nature, however, proceeds at very low reaction rates.

Recently, the feasibility of such a reaction in process plants has been studied. These studies mainly aim at increasing the reaction rate.

At the internet site of the US department of energy, http://www.fetc.doe.gov/publications/factsheets/program/-prog006.pdf, for example, is disclosed the reaction of finely ground serpentine ($Mg_3Si_2O_5(OH)_4$) or olivine (Mg_2SiO_4) in a solution of supercritical carbon dioxide and water to form magnesium carbonate. Under conditions of high temperature and pressure, 84% conversion of olivine has been achieved in 6 hours and a 80% conversion of pre-heated serpentine in less than an hour.

Other studies focus on the process of molten salt carbonation of mineral silicates with molten $MgCl_2$. This process is described by Walters et al. at the internet site hppt:\\www.netl.doe.gov/products/gcc/indepth/-mineral/minarb.html, and comprises the formation of magnesium hydroxide from magnesium silicates, via the formation of $MgCl_2$ using concentrated hydrochloric acid followed by hydrolysis of $MgCl_2$. Magnesium hydroxide is then carbonated in a direct gas solid reaction with carbon dioxide.

The above-mentioned processes, however, involve either the use of supercritical carbon dioxide or of concentrated hydrochloric acid. There is a need in the art for a rapid mineral carbonation process without the need of the use of supercritical conditions or of harmful or corrosive chemicals such as hydrochloric acid.

It has now been found that it is possible to react carbon dioxide with mineral silicates at an acceptable reaction rate if the reaction is performed with silicates that are immersed in an aqueous electrolyte solution.

Accordingly, the present invention relates to a process for mineral carbonation with carbon dioxide wherein carbon dioxide is reacted with a bivalent alkaline earth metal silicate, selected from the group of ortho-, di-, ring, and chain silicates, which silicate is immersed in an aqueous electrolyte solution.

In the process according to the invention, carbon dioxide is brought into contact with an aqueous electrolyte solution wherein the silicate is immersed. It will be appreciated that under such conditions, part of the carbon dioxide will dissolve in the aqueous solution and part will be present in the form of HCO_3^- or CO_3^{2-} ions.

Carbon dioxide may be brought into contact with the aqueous electrolyte solution wherein the silicate is immersed in any reactor suitable for gas-solid reactions in the presence of a liquid. Such reactors are known in the art. Examples of suitable reactors are a slurry bubble column or an extruder.

The ratio of mineral silicate to aqueous electrolyte solution depends inter alia on the type of reactor used, the particle size of the silica and process conditions like temperature and pressure.

In order to achieve a high reaction rate, it is preferred that the carbon dioxide concentration is high, which can be achieved by applying an elevated carbon dioxide pressure. Suitable carbon dioxide pressures are in the range of from 0.05 to 100 bar (absolute), preferably in the range of from 0.1 to 50 bar (absolute).

The total process pressure is preferably in the range of from 1 to 150 bar (absolute), more preferably of from 1 to 75 bar (absolute).

It is preferred that the silicate immersed in the electrolyte solution is in the form of small particles in order to achieve a high reaction rate. Particles having an average diameter of at most 5 mm may suitably be used. Preferably, the average diameter is at most 1 mm, more preferably at most 0.2 mm. Preferably, the average diameter is not smaller than 10 μm in order to avoid a very high energy input needed for particle size reduction.

Reference herein to the average diameter is to the volume medium diameter D(v,0.5), meaning that 50 volume% of the particles have an equivalent spherical diameter that is smaller than the average diameter and 50 volume% of the particles have an equivalent spherical diameter that is greater than the average diameter. The equivalent

spherical diameter is the diameter calculated from volume determinations, e.g. by laser diffraction measurements.

It has been found that the reaction rate can be further increased when the silicate particles are reduced in size during the process. This can be achieved by a process wherein the particles are mechanically broken up into smaller particles, for example by an extrusion, kneading or wet-milling process.

Alternatively, the process according to the invention may be carried out by injecting carbon dioxide together with an aqueous electrolyte solution into underground layers that contain mineral silicates.

Suitable silicates for the process according to the invention are ortho-, di-, ring, and chain silicates.

Silicates are composed of orthosilicate monomers, i.e. the orthosilicate ion $SiO_4{}^{4-}$ which has a tetrahedral structure. Orthosilicate monomers form oligomers by means of O-Si-O bonds at the polygon corners. The Q^s notation refers to the connectivity of the silicon atoms. The value of superscript s defines the number of nearest neighbour silicon atoms to a given Si.

Orthosilicates, also referred to as nesosilicates, are silicates which are composed of distinct orthosilicate tetrathedra that are not bonded to each other by means of O-Si-O bonds (Q^0 structure). An example of an orthosilicate is forsterite. Disilicates, also referred to as sorosilicates, have two orthosilicate tetrahedra linked to each other ($Si_2O_7{}^{6-}$ as unit structure, i.e. a Q^1Q^1 structure). Ring silicates, also referred to as cyclosilicates, typically have $SiO_3{}^{2-}$ as unit structure, i.e. a $(Q^2)_n$ structure. Chain silicates, also referred to as inosilicates, might be single chain

(SiO_3^{2-} as unit structure, i.e. a $(Q^2)_n$ structure) or double chain silicates ($(Q^3Q^2)_n$ structure).

Phyllosilicates, which are silicates having a sheet structure $(Q^3)_n$, and tectosilicates, which have a framework structure $(Q^4)_n$, are not suitable for the process according to the invention.

The silicates suitable for the process of the present invention are bivalent alkaline earth metal silicates, preferably calcium and/or magnesium silicates. Other metal ions, such as iron, aluminium, or manganese ions, may be present besides the bivalent alkaline earth metal ions. Especially in naturally-occurring silicates, both bivalent alkaline earth metal ions and other metal ions are present. An example is olivine which contains bivalent iron ions and magnesium ions. Examples of calcium and/or magnesium silicates suitable for the process according to the invention are forsterite, olivine, monticellite, wollastonite, diopside, and enstatite.

The aqueous electrolyte solution in which the silicate is immersed is preferably a solution of a salt that has a solubility in water of at least 0.01 moles per litre at 298K and 1 atmosphere, preferably at least 0.1 moles per litre. Preferred salts are sodium, potassium or barium salts, more preferably chlorides or nitrates of sodium, potassium or barium salts, i.e. $NaCl$, KCl, $BaCl_2$, $NaNO_3$, KNO_3, or $Ba(NO_3)_2$, even more preferably sodium nitrate.

The electrolyte solution suitably has an electrolyte concentration of at least 0.01 moles/litres, preferably in the range of from 0.1 to 2 moles per litre.

The process according to the invention is preferably performed at elevated temperature. It will be appreciated

that the maximum temperature is determined by thermodynamic considerations. If calcium silicate is used, suitable temperatures are typically in the range of from 20 to 400 °C, preferably in the range of from 80 to 300 °C, more preferably of from 100 to 200 °C. If magnesium silicate is used, suitable temperatures are typically in the range of from 20 to 250 °C, preferably of from 100 to 200 °C.

The process according to the invention can suitably be used to remove carbon dioxide from natural gas. Thus, in a specific embodiment of the invention, carbon dioxide-containing natural gas is contacted with an aqueous electrolyte solution wherein silicate is immersed. If the natural gas is already available at elevated pressure, there is no need to depressurise the gas before reacting it with silicate.

The mixture of carbonate and silica formed by the process of the invention can be disposed of, for example by refilling mining pits. It is, however, advantageous to form products from it having a commercial value.

In a further aspect of the invention, the mixture of carbonate and silica formed is used in construction materials. Examples of construction materials that can be produced from such a mixture are solid construction elements like building blocks, paving stones and roofing tiles composed of solid mineral particles and a binder as described in WO 00/46164. Such materials typically comprise from 70 to 99% by weight of solid particles and from 1 to 30% by weight of binder. These materials are typically manufactured by mixing the solid particles with the molten binder and allowing the mixture to solidify. Suitable binders are commercially available. Hydrocarbonaceous binders such as described in WO 00/46164 are particularly suitable.

In a still further aspect, the invention relates to the use of the carbonate formed for the manufacture of calcium oxide. It is well-known to produce calcium oxide from carbonates. A disadvantage, however, of the manufacture of calcium oxide from carbonates obtained by mining is that the overall process is carbon dioxide producing. By using the carbonate formed in the carbonation process as hereinbefore described, the overall process is a carbon dioxide neutral process with respect to the stoichiometry of the reactions involved. In the manufacture of calcium oxide according to the invention, the carbonate may be used as a mixture with silica.

If carbonate and/or silica is separately desired, the products of the carbonation process of the invention can be separated by technologies known in the art, for example by density separation such as sink-flotation.

The process of the invention will be illustrated by means of the following examples.

EXAMPLE 1

Experiment 1 (according to the invention)

Wollastonite ($CaSiO_3$) powder having an average diameter (D(v, 0.5)) of 61 μm as measured by laser diffraction, was immersed in a solution of NaCl (0.04 g/ml) in water. The wollastonite concentration was 0.077 g/ml. The thus-obtained wollastonite slurry was brought, in a stirred autoclave, to a temperature of 180 °C and a pressure of 40 bar g. Carbon dioxide in an amount such that the pressure remained constant was continuously fed to the autoclave. Conversion was determined after one hour and after 3 hours reaction time by taking a sample of the slurry and measuring the weight loss after heating the dry reaction product at 900 °C and comparing the

weight loss to the theoretic maximum loss that would be achieved at 100% conversion.

Experiment 2 (comparative)

An experiment similar to experiment 1 was performed, but without NaCl in the wollastonite slurry.

EXAMPLE 2

Experiment 3 (according to the invention)

A slurry of 5 grams of fine wollastonite powder, having an average diameter (D(v, 0.5)) of 13 μm as measured by laser diffraction, in 50 ml of an aqueous NaCl solution (0.06 g/ml) was loaded into a glass flask. The slurry was brought to a temperature of 100 °C at ambient pressure. A mixture of nitrogen and carbon dioxide (50/50 v/v) was bubbled through the slurry at a rate of 12 ml per minute. After 16 hours reaction time, the conversion was determined as described in experiment 1.

Experiment 4 (comparative)

An experiment similar to experiment 3 was performed, but without NaCl in the wollastonite slurry.

The results of the conversion measurements in experiments 1 to 4 are shown in the Table below.

TABLE

	NaCl conc. (moles/litre)	Conversion (%)		
		1h	3h	16h
Experiment 1	0.68	62	76	
Experiment 2	-	46	53	
Experiment 3	1.0			52
Experiment 4	-			22

CLAIMS

1. A process for mineral carbonation with carbon dioxide wherein carbon dioxide is reacted with a bivalent alkaline earth metal silicate, selected from the group of ortho-, di-, ring, and chain silicates, which silicate is immersed in an aqueous electrolyte solution.

2. A process according to claim 1, wherein silicates particles are dispersed in the aqueous electrolyte solution.

3. A process according to claim 2, wherein the silicate particles have an average diameter of at most 5 mm, preferably at most 1 mm, more preferably at most 0.2 mm.

4. A process according to claim 2 or 3, wherein the silicate particles are mechanically treated such that their size is reduced during the process.

5. A process according to claim 4, which is an extrusion process.

6. A process according to any one of the preceding claims, wherein the electrolyte is a salt having a solubility in water of at least 0.01 moles per litre, preferably at least 0.1 moles per litre.

7. A process according to claim 6, wherein the electrolyte is a sodium, potassium or barium salt, more a chloride or nitrate of sodium, potassium or barium, even more preferably sodium nitrate.

8. A process according to any one of the preceding claims, wherein the concentration of electrolyte in the electrolyte solution is at least 0.01 moles per litre, preferably in the range of from 0.1 to 2 moles per litre.

9. A process according to any one of the preceding claims, wherein the bivalent alkaline earth metal silicate is a magnesium or calcium silicate.

10. A process according to claim 9, wherein the silicate is a calcium silicate and the operating temperature is in the range of from 20 to 400 °C, preferably of from 80 to 300 °C, more preferably of from 100 to 200 °C.

11. A process according to claim 9, wherein the silicate is a magnesium silicate and the operating temperature is in the range of from 20 to 250 °C, preferably of from 100 to 200 °C.

12. A process according to any one of the preceding claims, wherein the operating pressure is in the range of from 1 to 150 bar (absolute), preferably of from 1 to 75 bar (absolute).

13. Use of the mixture of silica and carbonate formed by the process according of any one of the preceding claims in construction materials.

14. A process according to any one of claims 1 to 12 further comprising mixing the mixture of silica and carbonate formed with a molten binder and solidifying the silica/carbonate/binder mixture a construction material.

15. A process according to claim 14, wherein the binder is a hydrocarbonaceous binder.

16. Use of the carbonate formed by the process according of any one of claims 1 to 12 for the production of calcium oxide.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/04336

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01F11/18 C01B33/12 C04B14/02 C04B26/26 C04B2/10
C08L95/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01F C01B C04B C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 46149 A (GRONCHI PAOLO ;CASSAR LUIGI (IT); ITALCEMENTI SPA (IT); MARCO TIZI) 10 August 2000 (2000-08-10) page 9, paragraph 2	13-15
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A		1-12

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 September 2002	11/09/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Zalm, W

INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 197651 Derwent Publications Ltd., London, GB; Class L02, AN 1976-94982X XP002177996 & JP 51 125414 A (OSAKA PACKING SEIZOSHO KK), 1 November 1976 (1976-11-01) abstract ---	
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A	WO 00 46164 A (REYNHOUT MARINUS JOHANNES ;SHELL INT RESEARCH (NL)) 10 August 2000 (2000-08-10) cited in the application the whole document ----	13-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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